

Fig. 1 — E.m.f. versus time traces (1-5) for the systems (1-5) (see text) respectively

observed which is probably associated with the instrument. Experiments have shown that the frequency in the above cases depends on the concentration of H_2SO_4 , KBrO_3 , Ce^{4+} or Mn^{2+} and the organic substrate and temperature³⁻⁵. In some cases it depends on time. The periodic curves in Fig. 1 can be regarded as made up of simple harmonic curves of definite amplitudes, phases and periods. The wavelengths of the components are in the ratios $\lambda:\lambda/2:\lambda/3:\dots$, so that their frequencies are in the ratio $w:2w:3w:\dots$.

It should be noted that the number of harmonics can be ascertained by Fourier analysis provided there is not anharmonicity. Very often relaxation oscillations are observed in Belousov-Zhabotinskii reagent and the task would become difficult.

One may expect a relation between the number of harmonics and the number of redox couples. Detailed mechanistic examination is necessary to establish such a relationship.

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TABLE 1 — FOURIER ANALYSIS OF THE SYSTEMS (1) to (5)

Reaction system*	Fourier series	Number of significant harmonics	Frequencies present
(1)	$y = 4.8 + 1.16 \sin wt - 5.6 \sin 2wt + 3.7 \sin 3wt \dots 4.2 \cos wt + 0.5 \cos 2wt - 1.04 \cos 3wt + \dots$	3	$w, 2w, 3w$
(2)	$y = 6.09 - 2.1 \sin wt - 5.5 \sin 2wt \dots + 0.2 \sin 3wt + 0.7 \sin 4wt \dots + 6.14 \cos wt - 0.5 \cos 2wt + 0.2 \cos 3wt - 0.3 \cos 4wt + 1.0 \cos 5wt + \dots$	4	$w, 2w, 4w, 5w$
(3)	$y = 6.5 - 8.3 \sin wt - 2.76 \sin 2wt - 1.65 \sin 5wt - 1.2 \sin 7wt \dots$	4	$w, 3w, 5w, 7w$
(4)	$y = 6.5 + 7.6 \sin wt + 3.8 \sin 2wt + 2.5 \sin 3wt + 1.9 \sin 4wt + 1.5 \sin 5wt \dots + 7.0 \cos wt + 1.76 \cos 2wt + 0.78 \cos 3wt + 0.44 \cos 4wt + 0.3 \cos 5wt + \dots$	5	$w, 2w, 3w, 4w, 5w$
(5)	$y = 5.7 + 2.4 \sin wt + 0.14 \sin 2wt - 1.8 \sin 3wt - 0.6 \sin 4wt + 1.5 \sin 5wt + 3.7 \sin 6wt + \dots - 0.5 \cos wt - 9.9 \cos 2wt - 2.6 \cos 3wt + 2.5 \cos 4wt + 4.3 \cos 5wt \dots$	5	$w, 2w, 3w, 4w, 5w$

*See text.

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Studies on Thermo-osmosis of NaCl & K_2SO_4 Solutions

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Hydrodynamic permeability and thermo-osmotic permeability of different solutions of sodium chloride and potassium sulphate have been measured through pyrex membranes impregnated with copper ferrocyanide. It has been found that hydrodynamic permeability remains the same for different solutions of the same electrolyte but thermo-osmotic permeability changes significantly. It decreases with increasing concentration of the electrolyte.

THERMO-OSMOSIS is of immense biological interest since it has been pointed out that in some plant tissues water flows from warmer side to the colder side indicating that thermo-osmosis might play an important role in biological mobilization of fluids^{1,2}. Thermo-osmosis of liquids has been studied by many workers³⁻⁷ and a thermodynamic theory of the same has been developed. Thermo-osmosis of liquid mixtures has also been studied very recently^{8,9}. Thermo-osmosis of electrolytes has, however, been given little attention so far. Carr and Sollner¹⁰ have carried some experiments and have come to the conclusion that thermo-osmosis is an electrochemical phenomenon related to electro-osmosis. However, sufficient reliable experimental data have not been provided so far to settle this point.

In this paper thermo-osmosis of sodium chloride and potassium sulphate has been studied and the dependence of thermo-osmotic permeability on concentration examined.

We consider two compartments filled with solutions of same concentration separated by a membrane having pores whose diameters are small enough to avoid purely viscous flow. The two compartments are kept at two different temperatures T_1 and T_2 . Following methods of non-equilibrium thermodynamics, the dissipation function¹¹ can be written as

$$\phi = J_U \frac{\Delta T}{T} + J_S \Delta \mu_S + J_W \Delta \mu_W \quad \dots(1)$$

where the subscripts S and W denote respectively the solute and the solvent.

It is known that

$$\Delta \mu_W = \bar{V}_W (\Delta P - \Delta \pi) \quad \dots(2)$$

and

$$\Delta \mu_S = \bar{V}_S \Delta P + \frac{\Delta \pi}{\bar{C}_S} \quad \dots(3)$$

where \bar{C}_S is the average concentration. Introducing explicit expressions for $\Delta \mu_S$ and $\Delta \mu_W$ and rearranging, Eq. (1) can be written as

$$\phi = (J_W \bar{V}_W + J_S \bar{V}_S) \Delta P + \left(\frac{J_S}{\bar{C}_S} - J_W \bar{V}_W \right) \Delta \pi + J_U \left(\frac{\Delta T}{T} \right) \quad \dots(4)$$

\bar{V}_W and \bar{V}_S are the molar volumes of the solvent and the solute respectively. The total volume flow across the membrane is

$$J_V = (J_W \bar{V}_W + J_S \bar{V}_S) \quad \dots(5)$$

and hence

$$\phi = J_V \Delta P + J_D \Delta \pi + J_U \frac{\Delta T}{T} \quad \dots(6)$$

where J_D represents exchange flow.

Thus, the phenomenological equations can be written as

$$J_V = L_{11} \Delta P + L_{12} \Delta \pi + L_{1U} \left(\frac{\Delta T}{T} \right) \quad \dots(7)$$

$$J_D = L_{21} \Delta P + L_{22} \Delta \pi + L_{2U} \left(\frac{\Delta T}{T} \right) \quad \dots(8)$$

$$J_U = L_{U1} \Delta P + L_{U2} \Delta \pi + L_{UU} \left(\frac{\Delta T}{T} \right) \quad \dots(9)$$

In the condition of steady state when volume flow is zero

$$\left(\frac{\Delta P}{\Delta \pi} \right)_{J_V=0} = - \frac{L_{1U}}{L_{11}} \cdot \frac{1}{T} \quad \dots(10)$$

The explicit dependence of L_{1U} on pore size is not known. However, for gases L_{11} and L_{1U} can be shown to be proportional¹² to r^3 .

In earlier studies⁶ on thermo-osmosis, cellophane membranes were used. Possibility of deformation of the membrane when higher pressure difference was applied affected the reliability of the results. Hence pyrex sinter (G_4) was selected since it is sufficiently strong to withstand high pressure. However, as such it does not exhibit thermo-osmosis. This is due to the fact that pore size is much larger than that required for thermo-osmosis to occur. The size of the pores was reduced by impregnating copper ferrocyanide in the membrane.

Experimental procedure for measurement of hydrodynamic and thermo-osmotic permeability as described earlier^{8,9} was used. Average pore size of the membrane was measured and was found to be of the order of 10^{-6} cm. The thickness of the membrane was 0.25 cm and the area 7.98 cm².

From Fig. 1 it is evident that hydrodynamic permeability of water as well as solutions of sodium chloride in water is the same. The same is true for hydrodynamic permeability of potassium sulphate. This is in accordance with previous observation⁹. However, thermo-osmotic permeability decreases with increasing concentration of the electrolytes (Fig. 2). The values of thermo-osmotic coefficients are plotted as a function of concentration of the electrolyte in Fig. 3. The hydrodynamic coefficient for NaCl and K_2SO_4 solutions are 3.06 and 1.58 kg⁻¹ Sm⁴ in the concentration range 0.01M.

In order to assess whether any difference of concentration is developed during thermo-osmotic

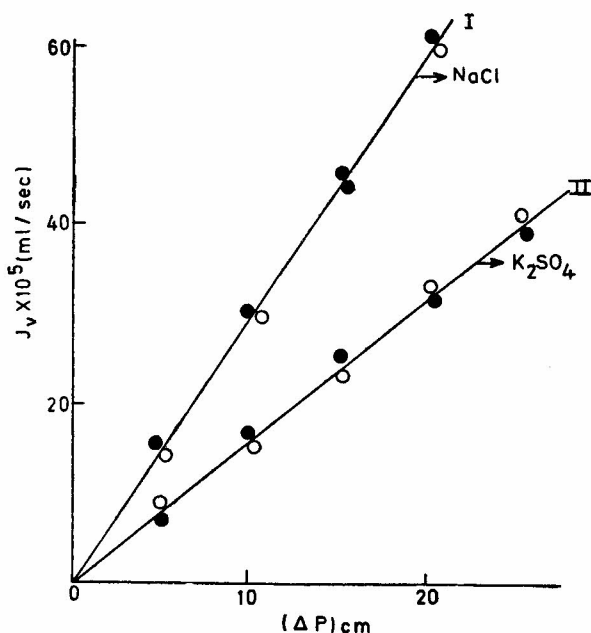


Fig. 1 — Hydrodynamic permeability of (I) water (○) and 0.025M NaCl solution (●); and (II) water (○) and 0.025M K_2SO_4 solution (●)

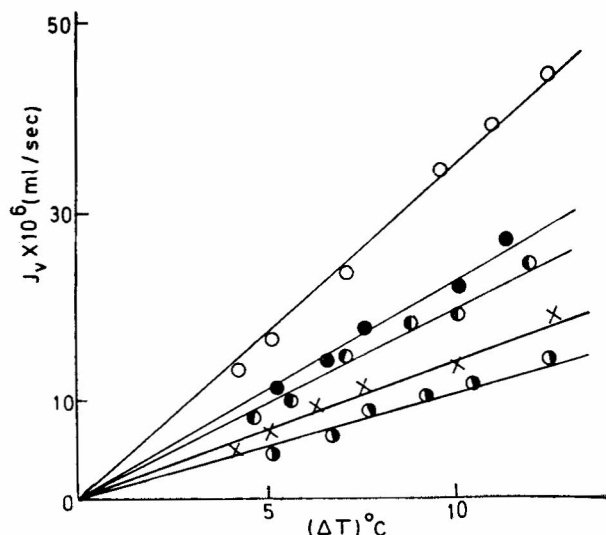


Fig. 2 — Thermo-osmotic permeability of solutions of sodium chloride in water [(○) water, (●) 0.025M, (◐) 0.050M, (×) 0.075M and (●) 0.100M sodium chloride]

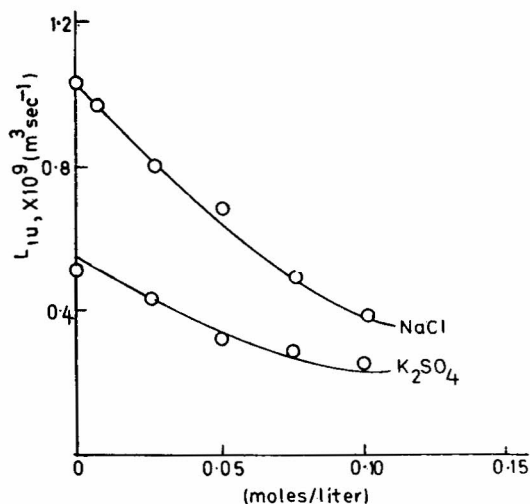


Fig. 3 — Plots of thermo-osmotic coefficient against concentration of the electrolytes

permeability measurement, density of the liquid on the two sides of the membrane was measured after steady state was reached. It was found that density remained practically constant, within experimental error. Density determinations were also made when the flow was allowed to take place under pressure gradient. Again the difference in density on the two sides of the membrane were found to be negligible. Hence it may be concluded that ΔC is negligible.

From these experiments it may be concluded that membrane does not possess semipermeability. This is due to the fact that membrane is not of copper ferrocyanide but of pyrex sinter impregnated with copper ferrocyanide.

It is apparent from Fig. 3 that thermo-osmotic permeability coefficient decreases continuously with increase in concentration of the electrolytes. Thermo-osmosis occurs when the mean free path is comparable to pore diameter, i.e. the thermo-osmotic flow

would be more if the molecules move without undergoing any collision. In the case of electrolytes, water ions are also carried away and they must be hydrated. When the concentration of the ions is increased, the chances of molecular collision during transport would increase and hence thermo-osmotic velocity would diminish with increase in concentration of the electrolytes. The hydrodynamic permeability on the other hand would not depend significantly on concentration of the electrolytes since the viscosity of the aqueous solutions of the electrolytes are not very much different.

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Enhancement of the Power Output of Photogalvanic Cells

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It is shown that the power output of photogalvanic cells is limited by their high internal resistance which cannot be reduced by reducing the ohmic resistance alone, e.g. by addition of inert electrolytes. To overcome this difficulty heterogeneous cells have been employed wherein an internal bias potential is provided by an appropriate redox couple in the dark compartment. The net power output obtainable in such cells is at least a factor of ten higher as compared with that obtainable in homogeneous cells hitherto employed. A few other advantages of the heterogeneous cell over the homogeneous one are also indicated.

INVESTIGATIONS of photoelectric chemical phenomenon have, in recent years, assumed great practical importance in view of their possible application to the direct conversion of solar energy into electricity. After the pioneering work of